J. of Supercritical Fluids 91 (2014) 37–45

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Extraction of jojoba oil with liquid CO_2 + propane solvent mixtures

C. Palla, P. Hegel*, S. Pereda, S. Bottini

Planta Piloto de Ingeniería Química, PLAPIQUI Universidad Nacional del Sur, CONICET, CC 717, 8000 Bahía Blanca, Argentina

ARTICLE INFO

Article history:
Received 13 December 2013
Received in revised form 4 April 2014
Accepted 8 April 2014
Available online 16 April 2014

Keywords:
Phase equilibria
Solubility
Jojoba oil
Extraction
Carbon dioxide
Propane

ABSTRACT

In this work liquid CO_2/propane mixtures were used to extract jojoba oil from oilseeds. First, experiments at 313 K and pressures of 70 bar and 200 bars were carried out on jojoba oil deposited on glass spheres, using different solvent concentrations (30 wt%, 50 wt% and 70 wt% CO_2), to assess the influence of the solvent composition and phase behavior on the extraction rate. Then, jojoba oil was extracted from the milled seeds under homogeneous liquid conditions, using solvent mixtures containing 30 wt% and 50 wt% CO_2 at 70 bar and 313 K. A solvent mixture with 30 wt% CO_2 exhibited good solvent power. Oil extraction yields of 98% were obtained using a minimum solvent to oilseed mass ratio of 5 g solvent/g oilseed and operating the extractor at 313 K and 70 bar.

1. Introduction

Jojoba oil is a liquid wax extracted from the seeds of the Jojoba plant (*Simmondsia chinensis*). Chemically, it is a mixture of high-molecular weight monounsaturated esters. Jojoba oil and oil derivatives have a wide range of industrial uses, mainly in cosmetics. They are commonly used in skin-care products, such as lotions, moisturizers, massage oils, and soothing creams. They are also used in the formulation of specialized lubricants, antifoaming agents, detergents, driers, emulsifiers, fibers, plasticizers, protective coating, resins and surfactants, among others [1].

Traditionally, jojoba oil is obtained by mechanical pressing, followed by hexane extraction of the pre-pressed jojoba meal. Health and environmental concerns associated with the use of solvents like hexane, have placed new demands on the cosmetic and pharmaceutical industry to invest in clean technologies such as supercritical fluid extraction.

The use of supercritical fluids for the extraction of oils from oilseeds has been widely studied in the literature [2–4]. Stahl et al. [5] and Salgın et al. [6,7] applied supercritical CO_2 ($scCO_2$) for the extraction of jojoba oil. Additionally, Salgın et al. [6,7] performed the extraction using co-solvents in order to increase the solubility of jojoba oil in $scCO_2$. CO_2 has been extensively studied [4] because it is an inert, inexpensive, easily available, odorless, tasteless and GRAS (Generally Recognized As Safe) solvent. As an additional advantage, CO_2 can be easily removed from the oil after extraction, by depressurization. However, the system jojoba oil + CO_2 is heterogeneous over a wide range of conditions, both under sub- and supercritical CO_2. High pressures are required to obtain good yields because the oil solubility in CO_2 is very low, even at pressures as high as 300 bar [6,7]. For this reason, the extraction of jojoba oil from its seed using$scCO_2$ is still not an attractive alternative from an economical point of view. On the other hand, although the use of ethanol as co-solvent can improve the performance of the extraction process, the drawback is that it remains in the oil after CO_2 depressurization and a complete removal of ethanol from the oil requires a vacuum step at low temperatures to avoid thermal degradation [8].

An alternative method for the extraction of jojoba oil from the seeds involves the addition of propane to carbon dioxide as solubility modifier. In general, vegetable oils are completely miscible with liquid propane at temperatures lower than ~343 K (LCEP). The solvent power of propane is much higher than that of CO_2, requiring less solvent/feed ratios and lower operating pressures. Also, propane can be easily removed from the oil after extraction by simple solvent depressurization. The main drawback of propane is its flammability. Any percentage of propane in a propane/air mixture higher than 2.15 vol.% will be sufficient for propane to burn [9]. This suggests that propane + CO_2 solvent mixtures may offer convenient properties regarding solvent power (greater affinity with the substrate than CO_2) and selectivity. On the other hand, mixtures with a 30/70 volume ratio of CO_2/propane in the vapor phase can be used to turn the propane/CO_2/air mixture non-flammable at ambient conditions [7]). Previous studies on vegetable oil extractions with propane + CO_2 mixtures have shown good results [3,10,11].

* Corresponding author. Tel.: +54 291 4861700; fax: +54 2914861600.
E-mail address: phegel@plapiqui.edu.ar (P. Hegel).

http://dx.doi.org/10.1016/j.supflu.2014.04.005
0896-8446/

In a previous work [8], an extraction process was proposed to extract jojoba oil using propane + CO_2 liquid mixtures at high pressure. The GC-EOS group contribution equation of state [12], combined with reliable experimental data (visual observations of phase transitions at different operating conditions), were used to study the phase equilibrium of CO_2 + propane + jojoba oil mixtures in order to choose the best operating conditions for the extraction process. The phase behavior of binary and ternary mixtures was studied at different temperatures, pressures and compositions, to determine conditions of good solvent power for non-flammable solvent mixtures. It was found that it is possible to avoid partial liquid miscibility when the jojoba oil extractor is operated at 70 bar and 313 K, with CO_2/propane solvent mixtures containing between 30 wt% and 50 wt% CO_2. Likewise, it is possible to increase the CO_2 concentration in the solvent mixture up to 70 wt%, at the expense of increasing the operating pressure in the extractor up to 200 bar, in order to keep homogeneous conditions and good solvent power [8].

In this work, experimental extractions of jojoba oil from milled seeds were carried out using CO_2/propane solvent mixtures in order to corroborate the previous study [8]. The influence of the solvent composition and the phase behavior on the extraction rate was analyzed. The solubility of jojoba oil in CO_2/propane mixtures at 313 K and different pressures was also determined from the experimental data in the present study. Special attention was given to the effect of heat pre-treatment and grinding size of the oilseeds, which have proved to influence the performance of the extraction process [6,7,13–15]. Different amounts of jojoba oilseed were processed in order to determine the solvent load capacity according to the CO_2 concentration in the solvent mixture. Additionally, a differential mass transfer model was used to fit the experimental data and to analyze the performance of the extractions.

2. Modeling

2.1. Mass transfer model

In order to model the extraction kinetics, a differential mass balance for the oil in the solid and fluid phases was implemented, as proposed by del Valle and de la Fuente [16]. Basically, the model assumes spherical particles, no-gradients of temperature and pressure in the solid bed, constant density and viscosity of the solvent mixture and axial plug flow with uniform interstitial velocity. The model also assumes a pseudo-equilibrium oil distribution between the solid and fluid phases, given by constant K (solute/matrix interaction). To solve the model equations, the axial and time variables were transformed into dimensionless quantities, in terms of the extractor height ($Z = z/H$) and residence time ($\tau = t/t_r$, where $t_r = H/U$). The spatial derivative term was represented by finite differences, transforming the partial differential equations into a set of ordinary differential equations. The final model for the extraction bed is represented by the following equations:

$$\frac{dY_i}{d\tau} = A(KX_i - Y_i) - \frac{(Y_{i+1} - Y_i)}{\Delta Z}, \quad A = \frac{h_f a_v H}{U\varepsilon} \tag{1}$$

$$\frac{dX_i}{d\tau} = B(KX_i - Y_i), \quad B = \frac{-h_f a_v \rho_f H}{U\rho_s(1-\varepsilon)} \tag{2}$$

In these equations Yi represents the oil concentration in the fluid phase (kg oil/kg solvent) and X_i the oil concentration in the solid phase (kg oil/kg inert solid matrix), for each i term of the spatial derivative. As mentioned before, τ and Z are dimensionless variables of time and space, respectively. K is a partition coefficient, the ratio of the initial oil concentration in the fluid and solid phases; h_f is the overall external mass transfer coefficient (m/s); H is the extractor height (m), ρ_f is the solvent density (kg/m^3), ρ_s is the inert solid density (kg/m^3), U is the interstitial solvent velocity (m/s) and a_v is the specific surface area per unit volume of extractor (m^2/m^3). This specific surface area is calculated as $a_v = 6(1-\varepsilon)/d_p$, where ε is the bed porosity and d_p is the particle diameter (m).

In order to solve the differential equations the following initial and boundary conditions were applied:

$$Y\big|_{Z=0} = 0, \quad X\big|_{\tau=0} = X_0, \quad Y\big|_{\tau=0} = Y_0 \tag{3}$$

where Y_0 is the initial oil concentration in the fluid phase and X_0 is the initial oil concentration in the solid phase after the dissolution of the oil in the solvent. These quantities were estimated from the definition of the partition coefficient and the initial mass balance of the solute:

$$X_0 = X_u - \frac{V\varepsilon\rho_f}{m}Y_0, \quad Y_0 = KX_0 = \frac{KX_u}{1 + V\varepsilon\rho_f K/m} \tag{4}$$

In Eq. (4), V represents the extractor volume, m is the mass of inert material (glass spheres + oil-free seeds) and X_u is the initial oil concentration in the solid phase, estimated from the ratio between the total amount of oil in the extractor and m.

Twenty terms of the spatial derivative were used to model axial plug flow pattern. The set of ordinary differential equations were solved numerically by the Runge–Kutta–Felhberg method [17] and the cumulative extraction curves were obtained by integrating the profiles of solute concentration at the extractor outlet using Simpson rule [17]. The values of the partition coefficient (K) and the overall mass transfer coefficient (h_f) were left as fitting parameters, obtained by adjusting the model to the experimental extraction curves.

2.2. Phase equilibria and physical properties

The group contribution equation of state (GC-EOS) [12] was used to determine the boundaries of the homogeneous region and to calculate the solubility of jojoba oil in the extract (light-liquid) phase in those extraction studies performed under conditions of partial liquid miscibility. The application of the model to mixtures of fatty oils with near-critical fluids is described in detail elsewhere [18]. The model parameters used in this work to model the phase behavior of the ternary system jojoba oil + propane + CO_2 were reported in a previous work [8].

The physical properties were estimated as follows. The density of the solvent mixture was estimated from the correlation of experimental data reported by Galicia Luna et al. [19] and Niesen et al. [20]. The solvent viscosity was calculated from the viscosity of the pure components at a given pressure and temperature, by applying the equation of Grunberg and Nissan [21]. Finally, the diffusion coefficient of jojoba oil in the solvent mixture was obtained from the equation of Perkins and Geankoplis [21] for multi-component mixtures. The binary diffusion coefficients of jojoba oil in pure CO_2 and in pure propane were in turn calculated by the correlation of Catchpole and King [22] as a function of the reduce temperature and density of the pure solvents. The solute molar mass (equal to 616.5 g/mol) was estimated from the fatty acid composition of jojoba oil, and the solute critical volume (equal to 2337.5 cm^3/mol) was calculated with Joback method [23]. Table 1 summarizes the values of the physical properties calculated by the correlations mentioned above.

Table 2, on the other hand, shows the overall external mass transfer coefficients estimated from the correlations applied in the literature for the supercritical extraction of vegetable oils [27], by using the properties reported in Table 1, a solvent flow rate of ~0.5 g/min and a specific surface area of 3600 m^2/m^3. It can be observed from Table 2, important differences in the estimation of the h_f parameter in the region of operating conditions studied in this work. Overall external mass transfer coefficients estimated

Table 1
Estimated values of the density (ρ_f) and viscosity (μ_f) of the solvent mixtures, and pseudo binary diffusion coefficient (D_{12}) of jojoba oil in these solvents at 313 K.

	Pressure					
	70 bar			200 bar		
	CO_2 weight fraction in solvent mixture					
	0.3	0.5	0.7	0.3	0.5	0.7
ρ_f (Kg/m^3)	550.5	563.4	537	586	598.4	572
μ (Pa s) 10^5	6.3	4.6	3.3	11.0	10.3	94.1
D_{12} (m^2/s) 10^8	1.0	1.4	2.1	0.5	0.5	0.6

from correlations lie within the range 10^{-6}–10^{-4} m/s. These results are showing.

3. Experimental

3.1. Materials

The jojoba seeds (*S. chinensis*) used in the experiments were cultured and harvested in La Rioja (Argentina). The oil composition was detailed in a previous work [8]. The moisture content of the oilseeds was 3.8%, as determined from AOCS Method Ca2c-25 [29]. The clean seeds were ground in a rotary mill to particles of diameters smaller than 2.83 mm. Where a reference is made to flour, this corresponds to the milled fraction having particle diameters smaller than 0.84 mm. In those assays in which the particle diameter is not mentioned, all the ground material was used. The oil content of the seeds was determined by Soxhlet extraction using technical grade hexane during 10 h, followed by solvent removal under vacuum in a rotary-evaporator. The oil content in the ground material and in the flour was 47.2 wt%.

CO_2 (99.9%) was purchased to Linde AG and propane (99%) was supplied by the gas company TGS (Bahía Blanca, Argentina).

3.2. Experimental apparatus and procedure

Experimental runs were performed in a high-pressure extraction apparatus (Fig. 1) described in detail elsewhere [30]. Propane/carbon dioxide liquid mixtures were used as solvent. These mixtures were prepared gravimetrically in a stainless steel cylinder (500 mL capacity) at a given mass ratio. The final solvent composition was analyzed by gas chromatography. The solvent compositions ranged from 30 wt% to 70 wt% CO_2, covering conditions of complete and partial liquid miscibility with the oil at operating temperatures and pressures. The solvent mixtures were stored in the cylinder under liquid–vapor equilibria at room temperature and the liquid phase was pumped to the extractor. The storage vessel exhibited small pressure fluctuations during the operation. The solvent compositions in the studies ranged from 30 wt% to 70 wt% CO_2, covering conditions of complete and partial liquid miscibility with the oil at 313 K and operating extraction

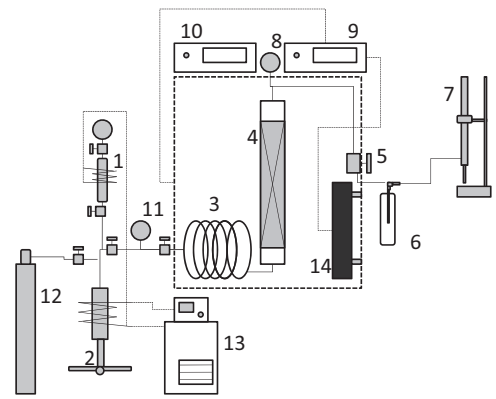

Fig. 1. (1) Gas stainless steel sample cylinder. (2) Pressure generator. (3) Heat exchanger element. (4) High-pressure extractor. (5) BPR valve. Extraction cell. (6) Liquid trap. (7) Flow-meter. (8) Extractor temperature sensor. (9) Temperature controller. (10) Extractor temperature indicator. (11) Pressure sensor. (12) Gas cylinder. (13) Low refrigerated circulator. (14) Heating element.

pressures. Chromatograph analyses of the solvent at the extractor outlet (HP 5890 – TCD detector – Porapack Q column) showed a variation of up to 2 wt% CO_2 for a given solvent mixture.

Two types of experiments were conducted to determine the oil solubility in the mixed solvent and to study the oil extraction from the milled seeds. The extraction procedure was as follows. A given amount of jojoba oil (1.5 g) or milled seeds (6 g or 11 g) were mixed with glass spheres (d = 1 mm). The extraction cell (46.5 ml capacity, 16.6 mm ID) was completely filled with the substrate. The bed porosity was assumed constant and equal to ε = 0.4 (it ranged between 0.398 and 0.406 depending on the relative mass of glass spheres and grounded seeds treated). After assembling the entire system, a gentle solvent stream was flushed through the cell to remove residual air. The extractor was then pressurized with the solvent mixture and left around 45 min to reach equilibrium at constant temperature and pressure (a longer period of static time of 90 min produced similar extraction results). Afterwards, the solvent was continuously pumped through the cell to carry out the oil extraction. After solvent depressurization in an outlet valve, the jojoba oil was collected in glass "U" tubes and weighed in a precision balance. The same solvent flow rate (0.5 ± 0.05 g/min) was adjusted to assure thermodynamic equilibrium (solubility measurements) and/or maximum solvent load (extraction experiments). The residence time in the cell filled with the substrate (glass spheres or glass spheres + grounded seeds) ranged between 20 min and 25 min, depending on the solvent density. The extraction equipment was operated as described above, at 313 K and pressures of 70–200 bar. Unequally time spaced samples (5–20 min) were taken in all cases during the total extraction time (100–140 min). Duplicated experiments showed variations in gravimetric yields of the cumulative extraction curves that were typically between 1 and 10% on a relative basis, according to the mass of extracted oil.

Table 2
Overall external mass transfer coefficients, h_f (m/s), estimated according to literature.

Authors	Pressure					
	70 bar			200 bar		
	CO_2 weight fraction in solvent mixture					
	0.3	0.5	0.7	0.3	0.5	0.7
Lee et al. [24]	4.2×10^{-6}	4.0×10^{-6}	4.8×10^{-6}	4.4×10^{-6}	4.0×10^{-6}	4.1×10^{-6}
Lee and Holder [25]	4.0×10^{-4}	5.6×10^{-4}	4.5×10^{-4}	2.3×10^{-4}	2.3×10^{-4}	2.4×10^{-4}
Wakao and Kaguei [26]	3.7×10^{-5}	5.3×10^{-5}	8.8×10^{-5}	1.9×10^{-5}	1.9×10^{-5}	2.1×10^{-5}
Puiggené et al. [27]	1.4×10^{-5}	2.0×10^{-5}	2.9×10^{-5}	7.0×10^{-6}	7.3×10^{-6}	7.8×10^{-6}
Sovová et al. [28]	6.6×10^{-6}	7.5×10^{-6}	1.0×10^{-5}	5.9×10^{-6}	5.5×10^{-6}	5.1×10^{-6}

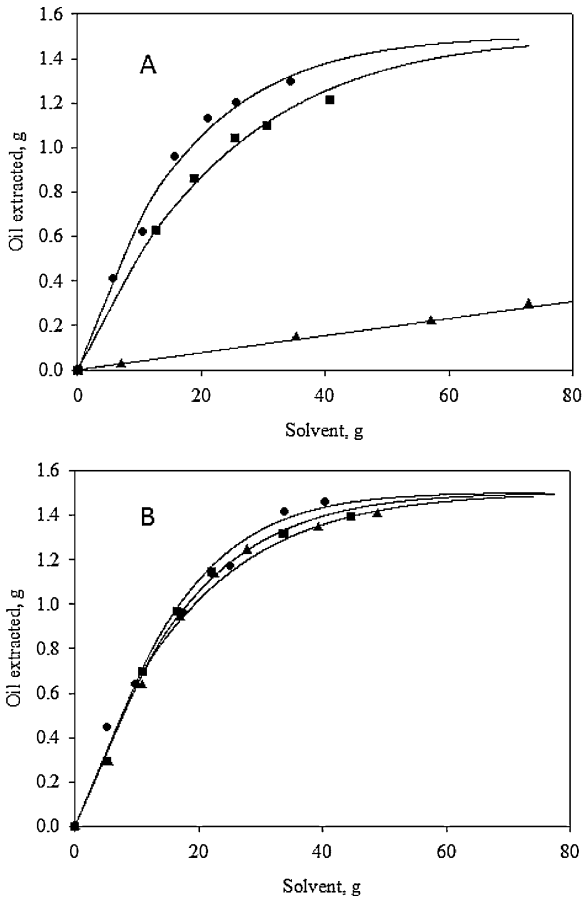

Fig. 2. Extraction of free jojoba oil with CO_2–propane solvent mixtures of different composition: (●) 30 wt% CO_2 (■) 50 wt% CO_2 and (▲) 70 wt% CO_2 at 313 K and 70 bar (A) or 200 bar (B), for a total oil content in the extractor of 1.5 g. Solvent flow = 0.5 g/min, symbols are experimental data. Lines are model fitting of experimental data, with the parameters reported in Table 3.

4. Results

4.1. Free-jojoba oil dissolution in CO_2/propane solvent mixtures

First, extractions of free-oil deposited on the glass spheres were carried out in order to determine the influence of pressure and solvent composition on the extraction rate, uncoupling any mass transfer effect on the vegetable matrix. Fig. 2 shows the cumulative extraction yield of jojoba oil as a function of the solvent mass, obtained at 70 bar (Fig. 2A) and 200 bar (Fig. 2B), using solvent mixtures with 30 wt%, 50 wt% and 70 wt% CO_2. The solvent mixtures having 30 wt% and 50 wt% CO_2 were able to extract nearly the entire oil content in the extractor after 80 min of extraction time (≈40 g of solvent mixture), independently of the operating pressure. The curves of lower CO_2 concentration in Fig. 2A show an initial steep increase and a plateau at the maximum oil yield, while the 70 wt% CO_2 solvent mixture exhibits a linear kinetic, which shows that only 20% of oil was removed after 112 min of operation (≈56 g of solvent). As it was found in previous work [8], this last solvent mixture exhibits partial liquid miscibility with jojoba oil at the conditions of the experiment, originating a poor solvent power restricted by the solubility limits.

As shown in Fig. 2B, when the pressure is increased up to 200 bar, all solvent mixtures present good solvent power, in correspondence with homogeneous conditions for all oil–solvent mixtures [10]. In this case the 30 wt% and 50 wt% CO_2 solvent mixtures depict a greater load capacity, related to the improvement of the transport properties due to the increase of the solvent density.

Table 3
Kinetic model parameters fitted from experimental data reported in Fig. 2 and initial oil concentration in the solvent mixtures at the extractor outlet.

Model parameters	Pressure					
	70 bar			200 bar		
	CO_2 weight fraction in solvent mixture					
	0.3	0.5	0.7	0.3	0.5	0.7
Y_0 (oil/solvent, g/kg)	68	52	3.9	66	64	60
K (–)	5.7	3.7	0.2	5.7	5.5	5.3
$h_f \times 10^7$ (m/s)	1.2	1.5	≥7	1.8	1.4	1.2

To sum up, extractions at homogeneous conditions allowed the highest extraction yield of jojoba oil. The 30 wt% CO_2 solvent mixture showed the best load capacity.

Table 3 reports the best-fitting parameters (K and h_f) that were used to adjust the experimental extraction curves and the Y_0 values obtained in the modeling. The values of K were obtained from the initial slope of the extraction curves, while h_f was determined from the last experimental points, where mass transfer problems prevail. A specific surface area of 3600 m^2/m^3 was considered in these studies for the estimation of h_f parameters. It can be observed, at the highest pressure, the Y_0 value was approximately constant for all the solvent mixtures studied (60–66, g oil/kg solvent), whereas the parameter showed a great variation at the lowest pressure. At 70 bar, an increment of CO_2 in the solvent up to 70 wt% produces a clear reduction of the apparent solubility due to liquid–liquid partial miscibility. Also, at this lower pressure there is a difference between Y_0 for the 30 wt% and 50 wt% CO_2 solvent mixtures. Different static time periods were tested (30 min, 60 and 90 min) with negligible effects on cumulative extraction curves. Therefore, this effect could be related to changes in the solvent transport properties and interfacial tension that could affect, for example, the wettability of the solvent + oil system and, in consequence, the rate of oil dissolution in the solvent during the extraction. The reduction in mass transfer rate with the CO_2 concentration observed at 70 bar could be related with the solvent non-ideality (theory of irreversible thermodynamics). It has been shown in a previous work [11] the oil activity at a given oil concentration in the solution increases with the CO_2/propane ratio in the solvent affecting the mass transfer properties.

The maximum oil concentration or solvent load capacity that can be attained in the extractor, Y_0^{max}, can be estimated theoretically assuming complete oil dissolution in the solvent during the static time. According to the initial mass of free-oil (1.5 g) and the mass of solvent loaded to the extractor at the different operating conditions (~10 g to ~11.1 g), the estimated Y_0^{max} values are between 135 and 150 g oil/kg solvent. There is an important difference between the estimated Y_0^{max} and the oil concentration observed at the extractor outlet in conditions of complete miscibility. This reduction in the solvent load can be related with high oil concentrations that modify solvent properties such as viscosity and interfacial tension affecting the normal dissolution. Also, this phenomenon can be associated with axial dispersion or hydrodynamic problems because of a high oil concentration that is affecting the normal axial plug flow. In fact, an intense mixing of the solution inside the extractor with the fresh solvent being pumped during the operation could takes place due to the low interstitial velocity or the long residence time of the solvent.

The values of the overall mass transfer coefficient, h_f, reported in Table 3 show variations according to the different operating conditions. Particularly, in the experiments at 200 bar the h_f value decreased with the CO_2 concentration in the solvent mixture and it

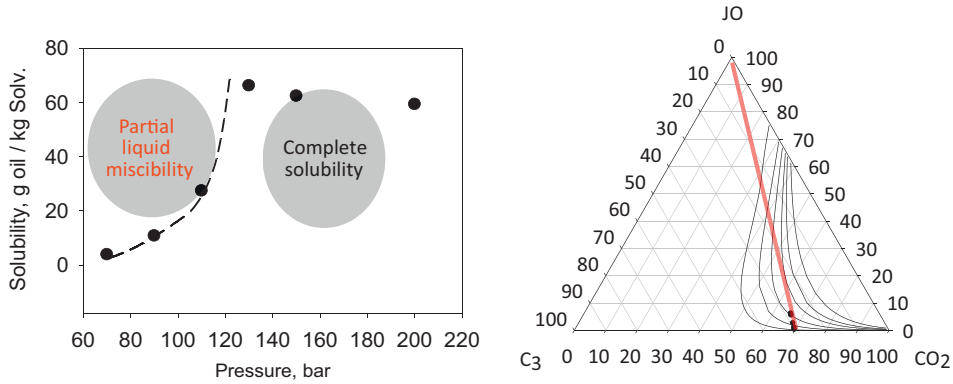

Fig. 3. Effect of pressure on the solubility of jojoba oil in a 70 wt% CO_2 solvent mixture at 313 K. (●) Experimental data measured in this work. Lines are GC-EOS modeling curves obtained in this work with parameters reported elsewhere [8].

presents an opposite behavior at the lower pressure. Also, a solvent mixture with 30 wt% CO_2 concentration showed a lower value of the h_f coefficient at 70 bar respect to the one obtained at the higher pressure. However, the values obtained from the extractions with 50 wt% CO_2 solvent mixtures were similar at both pressures. The h_f values are in general 1–2 orders of magnitude lower than those predicted from correlations of external mass transfer coefficients (see Table 2), which could also indicate the presence of hydrodynamic and axial dispersion effects. On the other hand, a value of h_f higher than 7×10^{-7} m/s was required to fit the experimental data obtained from the extractions with a 70 wt% CO_2 solvent mixture at 70 bar. This value, which is closer to the overall external mass transfer coefficients predicted from correlations, corresponds to fluid mixtures having a low concentration of oil due to the partial liquid miscibility present in the system.

Peclet numbers (*Pe*) based on the height of the packed beds estimated for the different operating conditions were lower than two (axial dispersion estimated from [31] for large-diameter particles) pointing out axial dispersion effects can be important [16]. It is worth mentioning that the mass transfer model proposed in this work can also be used with a single spatial derivative term to simulate a high degree of dispersion (ideal mixer) [32]. However, it is required experimental data obtained at different solvent flow rates to modeling properly the cumulative extraction curves taking into account the flow pattern (hydrodynamic problems) besides the overall mass transfer coefficient [32], which is out of the scope of this work. As example, an ideal mixer modeling of the extraction curves was tested showing that *K* values may increase being obtained initial oil concentrations $Y_0 = 100$ g oil/kg of solvent or greater, provided that the values of the h_f are lower than 10^{-7} m/s. Thus, it was decided modeling the extraction curves with a plug flow pattern because consistent model parameters were obtained to model the oil extraction from jojoba milled seeds. It should be understood that the model parameters in this case could be compensating the flow pattern due to the fluid dynamics of the system.

In general, the correlations normally used for supercritical CO_2 extractions [27] do not contemplate high oil concentrations in the fluid. Furthermore, interstitial velocities used to determine these correlations are higher than the ones used in this work [27]. A detailed study of the external mass transfer coefficients is beyond of the scope of this work.

4.2. Solubility of jojoba oil in a 70 wt% CO_2 solvent mixture

In order to determine in more detail the effect of partial liquid miscibility on the extraction process, the solubility of jojoba oil in a 70 wt% CO_2 solvent mixture was studied at 313 K and different pressures. The solubility was estimated from the linear part of the cumulative oil extraction curves plotted as grams of extracted oil vs. grams of solvent (as in Fig. 2). In the heterogeneous liquid–liquid region this value represents the thermodynamic solubility of jojoba oil in the solvent mixture. On the other hand, in the single fluid phase region the value of the slope is associated with transport properties and represents an apparent solubility, given by the solvent load capacity.

Fig. 3 illustrates the results of these experiments. The symbols in the figure represent the jojoba oil solubility in the light liquid phase at the extractor outlet, for a 70 wt% CO_2 solvent mixture at 313 K and for different operating pressures. The experimental results show an increase of oil solubility with pressure in the range of 70 bar to 130 bar. Beyond this point, the solubility decreases gradually with an increase in pressure. Under liquid–liquid equilibrium conditions, an increment in pressure causes an increase of solvent density, allowing a higher dissolution of jojoba oil in the solvent. On the other hand, in homogeneous systems the increase of solvent density produced by an increment of pressure implies a higher solvent mass in the extractor cell. For a given amount of oil charged initially into the extractor, this means a decrease of the apparent solubility. Thus, at 313 K the 70 wt% CO_2 solvent mixture attains complete miscibility with jojoba oil at 130 bar. At this pressure the maximum experimental solubility was 66.2 g jojoba oil/kg solvent. Stahl et al. [5] measured a jojoba oil solubility in pure CO_2 of 11 g jojoba oil/kg CO_2 at 350 bar and 333 K. On the other hand, Salgın et al. [6,7] determined a solubility of 15 g jojoba oil/kg CO_2 at 350 bar and 343 K and a solubility of 25 g jojoba oil/kg CO_2 when 8 vol% of ethanol was added as cosolvent. In this work it was found that the addition of 30 wt% of propane to CO_2 gives a solubility equal to 30 g jojoba oil/kg solvent operating at 110 bar and 313 K, under conditions of partial liquid miscibility. These results point out greater extraction efficiency of the mixed CO_2/propane solvent in comparison with pure CO_2 or CO_2 + ethanol mixtures, because it is possible to reach higher solubility operating the extractor at lower pressures. The triangular diagram and the dotted line in Fig. 3 are liquid–liquid equilibrium predictions by the GC-EOS model.

4.3. Experimental extraction of jojoba oil from milled seeds using CO_2/propane solvent mixtures

This section presents the results obtained in the case of the extraction of milled jojoba seeds with CO_2/propane solvent mixtures. The operating conditions were selected taking into account the results from the free-jojoba oil experiments presented in Section 4.1. The pressure was set at 70 bar, and two solvent compositions were tested at 30 wt% CO_2 and 50 wt% CO_2, carrying out the extractions under total liquid miscibility conditions. Different

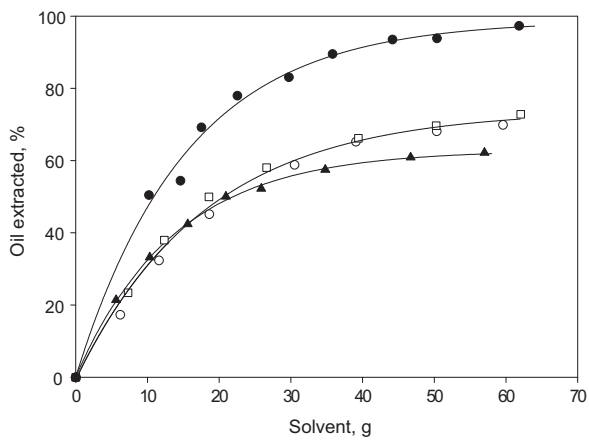

Fig. 4. Effect of the pretreatment on the percentage of jojoba oil extracted from seeds. Symbols are experimental data obtained in this work: (▲) untreated milled seeds ($dp = 1.5$ mm, $d < 2.8$ mm). (○) milled seeds ($dp = 1.5$ mm, $d < 2.8$ mm) preheated at 343 K, (□) milled seeds ($dp = 1.5$ mm, $d < 2.8$ mm) preheated at 363 K, (●) flour ($dp \approx 0.5$ mm, $dp < 0.84$ mm) preheated at 343 K. Experimental extraction conditions: 313 K, 70 bar, 30 wt% CO_2 solvent mixture and 0.05 g/min of solvent flow-rate. Lines: sketched for better visualization.

seed pretreatments were analyzed, looking for a maximization of the extraction yields.

It is worth mentioning that it is necessary to study the variability of the solvent load capacity with the CO_2 concentration in the solvent, in order to determine the makeup of propane that would be required in a process at pilot plant or industrial scale. It is considered in this work a minimum CO_2 concentration of 30 wt% to assure a non-flammable solvent mixture in the extraction, as well as in the solvent separation and recycling stages of the process. A solvent leakage would produce a gas with CO_2 concentrations greater than 30 V/V% which is non-flammable [7]. On the other hand, the solvent will be enriched in CO_2 along the extraction process, because in the oil/solvent separation step the oil will retain more propane than CO_2, so the concentration of the solvent recycle will change and the global solvent concentration in the extractor will be modified accordingly. The solvent retained in the jojoba oil extract can be easily stripped in a packed column operated with gaseous CO_2 at ambient temperature.

4.3.1. *Effect of heat pre-treatment and particle size*

Fig. 4 shows the cumulative extraction curves obtained from the extractions of jojoba seeds subject to different pretreatments. The experiments were carried out at 70 bar and 313 K using a 30 wt% CO_2 solvent mixture. In the first studies milled seeds with average diameter of 1.5 mm ($dp \leq 2.8$ mm) were used. Compared to the free jojoba oil extractions, in this case only 62 wt% of the total oil content could be extracted. Fig. 5 shows SEM images of the milled seeds surface before and after the extraction process. There is a great difference in the appearance of the material. Fig. 5B shows that free oil was nearly completely removed from the surface (although some brightness could be associated with remaining free oil). However, the cell structure in the solid matrix seems intact what would inhibit a clear contact between the solvent and the inner oil.

Different seed pretreatments were tested in order to maximize the extraction yields. First, a heat treatment was performed on the milled seeds, prior to extraction. It is expected that the cooking process will coagulate the proteins causing a coalescence of oil droplets and making also the seed more permeable to the flow of oil by decreasing the affinity of the oil to the solid matrix [13]. An extraction was performed on milled seeds having an average diameter of 1.5 mm ($dp \leq 2.8$ mm), preheated at 343 K. The extraction at 70 bar and 313 K with a 30 wt% CO_2 mixed solvent, showed an increase in the percentage of oil extracted from 62% to 69.9%. A preheating at 363 K did not produce any further increment in the extraction yield. It is concluded that heat treatment facilitates the release of oil from the material surface but do not promote the extraction of the oil from within the cell structure.

Further extractions were carried out to study the effect of particle size. For this purpose the flour portion of the milled seeds (particles with diameters smaller than 0.84 mm), preheated at 343 K, was extracted with a 30 wt% CO_2 solvent mixture at 313 K and 70 bar. Fig. 4 shows that in this case it was possible to obtain an oil yield of 99%. Salgın et al. [6] attributes the effect of particle size to intraparticle diffusion, which seems to gain importance in larger particles, causing an appreciable decrease in the extraction yield. In addition, Reverchon et al. [14] point out the effect of the change in the solvent-seed contact area. Fig. 6 shows that size reduction of the seeds in this case is also producing clear fractures in the material that releases the oil initially encapsulated in the cells.

The pretreatment efficiency was remarkable, because it made possible to obtain an extraction oil yield of 99% using a solvent/seed ratio of 10 g solvent/g seed. In comparison with previous work [5–7], the use of mixed CO_2/propane solvent showed a higher efficiency; for a given specific solvent/seed mass ratio a higher oil extraction yield was obtained.

4.3.2. *Effect of the CO_2 concentration in the solvent mixture*

In these experiments, different amounts of flour ($dp \approx 0.5$ mm), preheated at 343 K, were processed in the extractor, mixed with glass spheres ($dp = 1$ mm). Fig. 7A and B shows, respectively, the cumulative extraction curves obtained when 6 g and 11 g of jojoba flour were extracted with both solvent mixtures studied. The curves exhibit substantial differences in the extraction kinetics with the CO_2 concentration in the solvent mixture. For a specific solvent mass of 5 g CO_2/g seeds Fig. 7A shows that a yield barely higher than 60% (0.3 g oil/g seeds) was obtained with the 50 wt% CO_2 solvent mixture, while a yield of nearly 85% (0.4 g oil/g seeds) was reached

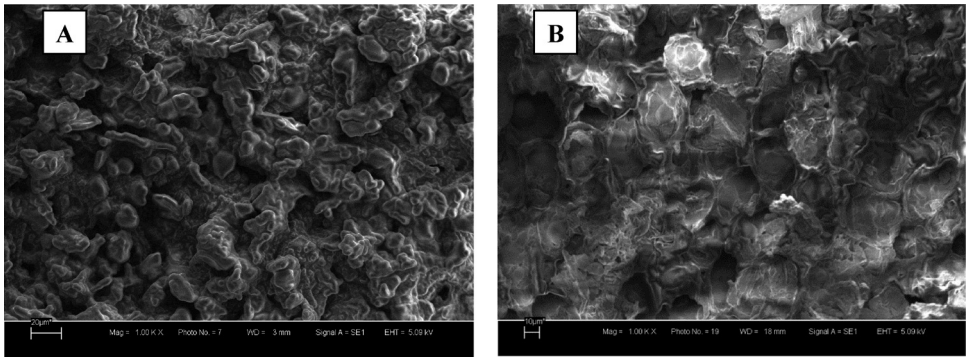

Fig. 5. Micrographs of jojoba ground seeds ($dp = 1.5$ mm, $dp < 2.8$ mm): (A) before and (B) after high pressure liquid extraction, at 1000× magnification.

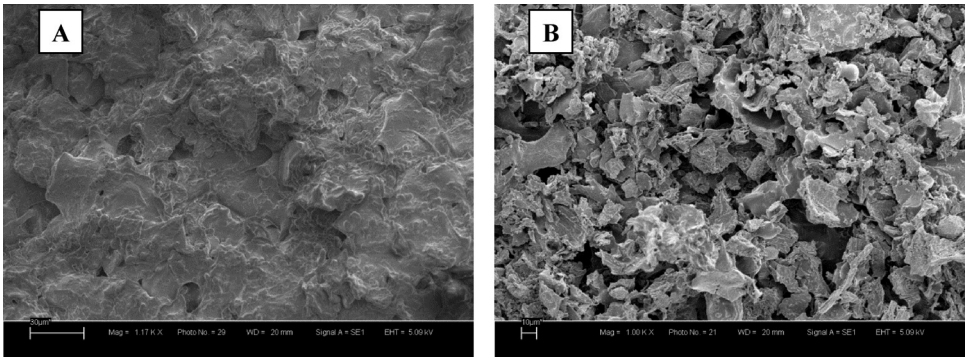

Fig. 6. Micrographs of jojoba flour ($dp \approx 0.5$, $dp < 0.84$ mm): (A) before and (B) after high pressure liquid extraction, at 1000× magnification.

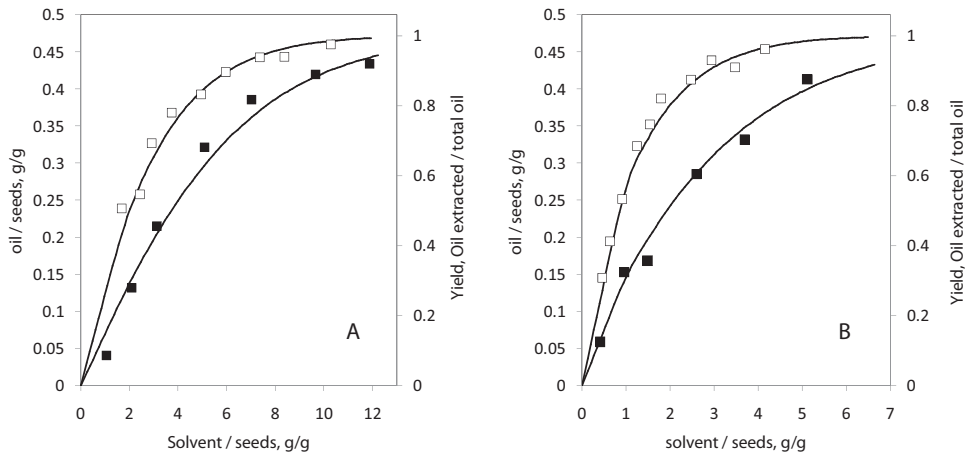

Fig. 7. Effect of solvent mixture composition on the percentage of jojoba oil extracted from milled seeds with particle diameter $d \approx 0.5$ mm and heat pretreatment at 343 K. (A) 6 g and (B) 11 g of seeds. Symbols are experimental data: solvent mixture with (□) 30 wt% CO_2 and (■) 50 wt %CO_2. Experimental extraction conditions: 313 K, 70 bar and 0.5 g/min of solvent flow-rate. Lines: best-fit lines obtained with the kinetic model parameters reported in Table 4.

for the solvent with 30 wt% CO_2. For the same specific solvent mass, the processing of 11 g of seeds gave almost complete oil extraction (0.46 g oil/g seeds) for the solvent with the lower concentration of CO_2 and 84% yield (0.4 g oil/g seeds) for the solvent with 50% CO_2 (see Fig. 7B).

For each solvent composition, Fig. 7 also illustrates an increase of the oil apparent solubility in the first part of the extraction, when greater amounts of milled seeds were processed. At the homogeneous working conditions of the experiments, this increment of the apparent solubility is related to the greater amount of oil loaded to the extractor for the same solvent mass quantity per unit of extractor volume.

Best-fit lines are also included in Fig. 7, and the corresponding values of the kinetic model parameters (K and hf) are reported in Table 4. The specific surface area, a_v, was modified to values of 4114 m^2/m^3 and 4800 m^2/m^3, according to the volumetric fraction of the grounded seeds mixed with the glass spheres (27 and 50 v/v%) and the mean seed particles diameter ($dp \approx 0.5$ mm). For each amount of seeds processed in the extractor (6 g and 11 g), the apparent solubility (and in consequence the value of K) decreased with the increment of CO_2 concentration in the solvent. On the other hand, for each solvent composition, the value of parameter K remained constant and independent of the amount of seeds processed, because the increase in the amount of substrate is followed by an increase of the apparent solubility. As an example, when 6 g of jojoba seeds were processed the initial oil concentration in the solid phase before the solvent was loaded to the extractor was $X_u = 52.5$ g oil/kg solid (50.8 g of glass spheres and 3.17 g of oil-free seeds), and it was observed from extractions carried out with a 30 wt% solvent mixture an initial apparent solubility of $Y_0 = 137$ g oil/kg solvent which reduced the oil concentration in the solid phase to $X_0 = 26.4$ g oil/kg solid in the first period of the extraction. The increment of the initial oil concentration in the solid phase to $X_u = 119.5$ g oil/kg solid (11 g of jojoba seeds – 37.8 g of glass spheres and 5.83 g of oil free seeds) rise the apparent solubility to $Y_0 = 280$ g oil/kg solvent and, according to a mass balance, the oil concentration in the solid phase at the extraction start was $X_0 = 53.8$ g oil/kg solid.

For the 30 wt% CO_2 mixed solvent, the value of K is closed to the one reported in Table 3 for *free-oil* extractions; this indicates a washing type behavior that takes place due to a great affinity between the solvent mixture and jojoba oil. The smaller K value obtained for the 50 wt% CO_2 solvent mixture indicates a lower solvent power to break the interaction between the oil and the vegetable matrix. At the same operating conditions, the overall mass transfer coefficient, h_f, obtained for mixed solvents with 30 wt% CO_2

Table 4
Kinetic model parameters fitted to the experimental data reported in Fig. 7 and initial oil concentration in the solvent mixtures at the extractor outlet.

Model parameters	Amount of jojoba oil seeds			
	6 g		11 g	
	CO_2 weight fraction in solvent mixture			
	0.3	0.5	0.3	0.5
Y_0 (oil/solvent, g/kg)	137.4	69.9	280	150
K (–)	5.2	1.8	5.2	1.8
$h_f \times 10^7$ (m/s)	0.9	2.6	0.7	1.1

showed a lower valued than the one obtained in the free-oil extractions. On the other hand, solvent mixtures with 50 wt% CO_2 showed h_f values closer to the ones reported on Table 3. These results are pointing out in general the presence of an internal mass transfer resistance in the extraction.

As it was mentioned previously, the low values of the h_f parameters could also compensate for dispersion or hydrodynamic problems that are not considered in the mass transfer model. This kind of phenomenon is likely to occur at higher amounts of oil processed in the extraction because high oil concentration gradients produce important changes in physical properties of the solution along the extractor. This effect can be seen in Table 4 from the parameters obtained for extractions carried out with a 50 wt% CO_2 solvent mixture where it takes place a great reduction of h_f with the mass of seeds treated.

The reduction of the solvent power at higher CO_2 concentrations can be explained by an increase of the solvent + oil non-ideality. According to a previous work [11], there is a dependence of the mass diffusivity with the oil concentration in the solvent which is related to the oil activity coefficient. This effect reduces the solvent power and is more significant at higher CO_2 concentrations.

The variation of the oil/solvent physical properties with the solvent composition could influence in general the solvent load capacity and transport properties [3]. According to Table 2, density and diffusivity practically remain constant with the solvent composition at a given pressure, while there is a significant change of viscosity with CO_2 concentration. Also, it is worth to mentioning that correlations used to estimate mass diffusivity [21,22] do not consider the dependence of the diffusion coefficient with oil concentration. The interfacial tension could be another important property. Hiller et al. [33] measured the interfacial tension in the systems linoleic acid/CO_2 and linoleic acid/ethane at 313 K and different pressures. Particularly, at 70 bar these authors determined an interfacial tension of 9.4 mN/m and 1.4 mN/m for the CO_2 and ethane binaries, respectively. Therefore, the variation of the CO_2 concentration in the solvent mixture could produce changes in the interfacial tension affecting the wettability of the solvent + oil mixture.

5. Conclusions

In this work high pressure liquid extractions of free-jojoba oil were carried out in order to analyze the effect of solvent composition (30–70 wt% CO_2), pressure (70 bar and 200 bar) and phase behavior on the solvent power. Extractions under liquid–liquid equilibrium conditions give low yields and should be avoided to prevent the restriction imposed on the solvent load capacity by the solubility limits. From the experimental results it can be concluded that it is possible to operate the extractor at 313 K and moderate pressures (~70 bar), using liquid CO_2/propane solvent mixtures having a minimum of 30 wt% CO_2 (to assure non-flammability) and up to 50 wt% CO_2 (to avoid partial liquid miscibility). The use of solvent mixtures with higher concentrations of CO_2 requires an increase of the operating pressure to reach homogeneous liquid conditions. For example a minimum of 130 bars is required for solvent mixtures with 70 wt% CO_2.

A heat pretreatment of the milled seeds at 343 K and a reduction of the particle size improved the extraction performance. Results obtained in the extraction of the flour portion ($dp < 0.84$ mm) of preheated milled seeds, carried out at 313 K and 70 bar with a 30 wt% CO_2 solvent mixture showed a similar cumulative extraction curve than that obtained from the free-oil experiments. In these experiments it was possible to extract up to 98% of the total oil content of seeds using 5 g solvent/g seeds. Lower extraction yields (up to 84%) were obtained with a 50 wt% CO_2 solvent mixture, for the same solvent/seed mass ratio.

The experimental cumulative extraction curves were fitted with a differential mass transfer model. The model showed a reduction of the partition coefficient for increasing CO_2 concentration in the solvent, revealing a lower affinity between solvent and jojoba oil even in conditions of complete miscibility.

Taking into account that the solvent will be enriched in CO_2 at the oil/solvent separation step, solvent recycling will increase the global concentration of CO_2 in the extractor. Extractions could be carried out with a 40 wt% CO_2 solvent mixture and a solvent make up having 30% CO_2 to reestablish the solvent load capacity.

Acknowledgements

This study was supported by grants from Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Universidad Nacional del Sur (UNS), Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT), and Comisión de Investigaciones Científicas de la Provincia de Buenos Aires.

References

[1] F. Shahidi (Ed.), Bailey's Industrial Oil and Fat Products. Volume 1. Edible Oils and Fat Products: Chemistry, Properties, and Health Effects, John Wiley & Sons, Inc., Hoboken, New Jersey, 2005.
[2] E. Stahl, K.W. Quirin, D. Gerard, Dense Gases for Extraction and Refining, Springer-Verlag, Berlin, 1988.
[3] J.W. King, G.R. List (Eds.), Supercritical Fluid Technology in Oiland Lipid Chemistry, AOCS Press, Champaign, IL, 1996.
[4] F. Temelli, Perspectives on supercritical fluid processing of fats and oils, J. Supercritical Fluids 47 (2009) 583–590.
[5] E. Stahl, K.W. Quirin, D. Gerard, Solubilities of soybean oil, jojoba oil and cuticular wax in dense carbon dioxide, Fette Siefen Anstrichmittel 85 (1983) 458–463.
[6] U. Salgın, A.C. Alımlı, B.Z. Uysal, Supercritical fluid extraction of jojoba oil, J. American Oil Chemists Society 81 (2004) 293–296.
[7] U. Salgın, Extraction of jojoba seed oil using supercritical CO_2 + ethanol mixture in green and high-tech separation process, J. Supercritical Fluids 39 (2007) 330–337.
[8] P. Hegel, G. Mabe, E.A. Brignole, S. Pereda, Phase equilibrium engineering of jojoba oil extraction with mixed CO_2 + propane solvents, J. Supercritical Fluids 79 (2013) 114–122.
[9] M.G. Zabetakis, Flammability characteristics of combustible gases and vapors. Bulletin 627 Bureau of Mines, Washington U.S. Dept. of the Interior, Bureau of Mines, 1965.
[10] P. Hegel, G. Mabe, S. Pereda, M.S. Zabaloy, E.A. Brignole, Phase equilibria of near critical CO_2 + propane mixtures with fixed oils in the LV, LL and LLV region, J. Supercritical Fluids 37 (2006) 316–322.
[11] P. Hegel, G. Mabe, S. Pereda, M.S. Zabaloy, E.A. Brignole, Phase equilibrium engineering of the extraction of oils from seeds using carbon dioxide + propane solvent mixtures, J. Supercritical Fluids 42 (2007) 318–324.
[12] S. Skjold-Jorgensen, Group contribution equation of state (GC-EoS): a predictive method for phase equilibrium computations over wide ranges of temperatures and pressures up to 30 MPa, Industrial & Engineering Chemistry Research 27 (1988) 110–118.
[13] B.D. Shukla, P.K. Srivastava, R.K. Gupta, Oilseed Processing Technology, Central Institute of Agricultural Engineering Publications, Bhopal, India, 1992.
[14] E. Reverchon, A. Kaziunas, C. Marrone, Supercritical CO_2 extraction of hiprose seed oil: experimental and mathematical modeling, Chemical Engineering Science 55 (2000) 2195–2201.
[15] S. Machmudah, Y. Kawahito, M. Sasaki, M. Goto, Supercritical CO_2 extraction of rosehip seed oil: fatty acids composition and process optimization, J. Supercritical Fluids 41 (2007) 421–428.
[16] J.M. Del Valle, J.C. de la Fuente, Supercritical CO_2 extraction of oilseeds: Review of kinetic and equilibrium models, Critical Reviews in Food Science and Nutrition 46 (2006) 131–160.
[17] K.E. Atkinson, An Introduction to Numerical Analysis, John Wiley & Sons, New York, 1989.
[18] S. Espinosa, T. Fornari, S.B. Bottini, E.A. Brignole, Phase equilibria in mixtures of fatty oils and derivatives with near critical fluids using the GC-EOS model, J. Supercritical Fluids 23 (2002) 91–102.
[19] L.A. Galicia-Luna, D. Richon, H. Renon, New loading technique for a vibrating tube densimeter and measurements of liquid densities up to 39.5 MPa for binary and ternary mixtures of the carbon dioxide–methanol–propane system, J. Chemical and Engineering Data 39 (1994) 424–431.
[20] V.G. Niesen, J.C. Rainwater, Critical locus, (vapor + liquid) equilibria, and coexisting densities of (carbon dioxide + propane) at temperatures from 311 K to 361 K, J. Chemical Thermodynamics 22 (1990) 717–795.

[21] B.E. Poling, J.M. Prausnitz, J.P. O'Connell, The Properties of Gases and Liquids, 5th ed., McGraw-Hill, New York, 2004.
[22] O.J. Catchpole, M.B. King, Measurement and correlation of binary diffusion coefficients in near critical fluids, Industrial and Engineering Chemistry Research 33 (1994) 1828–1837.
[23] K.G. Joback, R.C. Reid, Estimation of pure-component properties from group-contributions, Chemical Engineering Communications 57 (1987) 233–243.
[24] A.K.K. Lee, N.R. Bulley, M. Fattori, A. Meisen, Supercritical carbon dioxide extraction of canola oilseed in fixed beds, J. American Oil Chemists Society 63 (1986) 921–925.
[25] C.H. Lee, G.D. Holder, Use of supercritical fluid chromatography for obtaining mass transfer coefficients in fluid–solid systems at supercritical conditions, Industrial & Engineering Chemistry Research 34 (1995) 906–914.
[26] N. Wakao, S. Kaguei, Heat and Mass Transfer in Packed Beds, Gordon and Breach, New York, USA, 1982.
[27] J. Puiggené, M.A. Larrayoz, F. Recasens, Free liquid-to-supercritical fluid masstransfer in packed beds, Chemical Engineering Science 52 (1997) 195–212.
[28] H. Sovová, Rate of the vegetable oil extraction with supercritical carbon dioxide. I. Modelling of curves, Chemical Engineering Science 49 (1994) 409–414.
[29] Official Methods and Recommended Practices of the American Oil Chemists Society, Method Ca-2c-25, vol. 1, 4th ed., AOCS Press Campaign, Great Britain, 1993.
[30] N. Gañan, E.A. Brignole, Fractionation of essential oils with biocidal activity using supercritical CO_2 – experiments and modeling, J. Supercritical Fluids 58 (2011) 58–67.
[31] O.J. Catchpole, R. Bernig, Measurement and correlation of packed-bed xial dispersion coefficients in supercritical carbon dioxide, J. Supercritical Fluids 33 (2005) 35–52.
[32] H. Sóvova, Mathematical model for supercritical fluid extraction of natural products and extraction curve evaluation, J. Supercritical Fluids 33 (2005) 35–52.
[33] N. Hiller, H. Schiemann, E. Weidner, S. Peter, Interfacial tension in systems with a supercritical component at high pressures, Chemical Engineering & Technology 16 (1993) 206–212.